

Dissolution of embedded gold nanoparticles in sol–gel glass film

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Abstract

Materials with metallic nanoparticles are widely investigated in order to fabricate plasmonic devices, for which the control of the material properties is required. A simple way to control the metal surface plasmon resonance in selected regions of the material is to dissolve the embedded metallic nanoparticles by means of d.c. electric field. Dissolution of embedded silver and copper nanoparticles has been demonstrated recently through poling-assisted bleaching of Ag-doped and Cu-doped nanocomposite glasses, respectively. The next challenge is the dissolution of other metallic nanoparticles, such as gold, which are more difficult to ionize. Here, we demonstrate the dissolution of gold nanoparticles (15 nm in diameter) by d.c. electric field thanks to a novel material design in which the nanoparticles were embedded in a high resistivity sol–gel film on top of a soda-lime-silicate glass substrate with a higher conductivity compared to the film. The role of the film resistivity is made obvious by studying two different film compositions. This result brings about the possibility to use other metallic nanoparticles for tailoring the region of transparency of glasses and opens perspectives for the fabrication of new plasmonic devices.

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1. Introduction

Gold nanometer-size particles are used for a variety of applications based on the particles' surface plasmon resonance, leading to the development of plasmonic devices [1]. For instance, the fabrication of sub-wavelength optical devices [2] is useful for applications which require the miniaturization of optical components and a plasmonic waveguide operating at 1.55 μm wavelength was demonstrated based on a gold metal film embedded in SiO_2 [3]. Glasses doped with gold “nanoparticles” also present a high third-order nonlinear optical susceptibility [4] which can have a crucial role in the development of optical switches and waveguides. Whichever application is aimed at, in order to fabricate devices, it is necessary to control the material properties. A way to control the particle's surface plasmon resonance was discovered through the

electric-field-induced dissolution of silver [5] and copper [6] nanoparticles embedded in ion-conducting glasses and the subsequent bleaching of the metal-doped nanocomposite materials in a region delimited by the anode geometry. Recently, femtosecond-laser-induced dissolution of gold nanoparticles [7] was demonstrated as a tool to control the size of the gold nanoparticles anywhere inside the glass host.

Here, we present a new structure of gold nanoparticles embedded in a sol–gel film on top of a soda-lime-silicate glass, which can serve as a convenient optical material for the fabrication of plasmonic devices and for the modification of the spatial distribution of nanoparticles. In the present material structure, a sol–gel film of low electrical conductivity containing metal nanoparticles is coated on a highly conductive soda-lime glass substrate. Clearly, this sol–gel-embedded gold nanoparticle structure is different from the one reported for silver nanoparticles [5] where the nanoparticles were embedded in a soda-lime-silicate glass substrate by ion-exchange process and subsequent annealing. Through the simple and versatile thermal poling technique, we demonstrate that gold nanoparticles can be

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dissolved by d.c. electric field only if specific conductivity conditions are satisfied, which is achievable since both the resistivity and the thickness of the sol–gel film can be controlled at the stage of the fabrication process. As it is necessary to have high electric field strengths in order to ionize gold clusters, the control of the film thickness down to 100 nm allows the development of an extremely high electric field underneath the anodic surface due to poling. After poling, the glass colour could be bleached totally or partially under the anode due to a controlled change in the absorption of the nanocomposite material. Therefore, thermal poling is effectively used here to dissolve embedded gold nanoparticles and total suppression of the surface-plasmon-resonant absorption band related to the gold nanoparticles is demonstrated.

2. Experimental conditions

The nanocomposite film was formed by the sol–gel method through the deposition of a coating solution containing an organic silicon compound and a salt of gold onto a glass plate. The resulting film had a structure in which the nanoparticles were dispersed in the matrix of SiO_2 . Two different sol–gel film compositions (type #1 and type #2) on top of a 3-mm-thick substrate were investigated (Table 1). According to the film composition, the sample was coloured in either pink (type #1) or blue (type #2) as the increase of the host refractive index shifted the surface plasmon absorption peak frequency towards the red [8]. The volume fraction of gold was estimated to be 2.3% for the pink sample and 5.2% for the blue sample. The gold particle diameter was 15 nm for the pink sample and 8.5 nm for blue sample. Scanning Electron Microscope (SEM) image of the cross section of etched pink sample (Fig. 1) showed that the gold nanoparticles were randomly distributed within the sol–gel film, i.e. there was no gradient of the particle concentration across the depth. Iron oxide was also present in the substrate of type #1 (0.1 wt.%) and type #2 (0.6 wt.%) samples.

The 3-mm-thick samples with type #1 and type #2 sol–gel films were identically poled in an oven (280 °C, air atmosphere) up to 1 kV using pressed-contact steel electrodes (9×7 mm), with the sol–gel film top surface facing the anode. Due to the high ionic conductivity of the substrate, the same procedure used for poling soda-lime glass [9] was employed. Specifically, the voltage was increased by steps of 200 V (five steps in total) for a fixed period of time (10 min each step). During each step, the current was limited in order to avoid runaway. When the

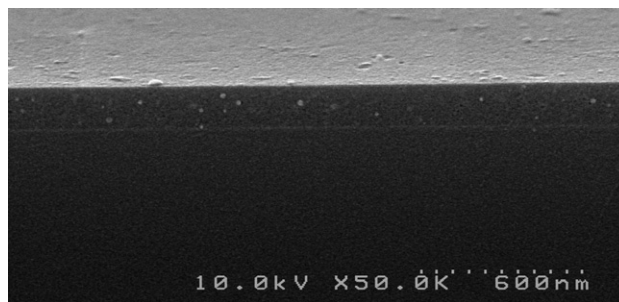


Fig. 1. SEM image of the cross section of etched pink sample (type #1) (magnification: 50,000×, tilt angle: 10°). The gold nanoparticles can be seen as white spots randomly distributed in the 130-nm-thick sol–gel glass film.

final poling voltage was reached, the sample was cooled down to room temperature while keeping the voltage applied.

3. Results and discussion

After poling the pink sample, a well-defined region of the sample, delimited by the anode geometry, became colourless. The bleaching observed in that region indicated that the gold nanoparticles were not present anymore since the original pink colour was due to the presence of these particles. This effect, i.e. poling-assisted bleaching, was observed previously in samples with silver nanoparticles embedded in soda-lime glass [5]. Contrary to what was observed in the pink sample, no bleaching was reported after poling the blue sample, although the poling conditions were strictly the same.

The temporal behaviours of the poling current in both types of samples (Fig. 2) gave us more insight on what happened during poling. Because the high-resistivity film faced the anode, there was no supply of external cations (blocking electrode). Similarly to the case of soda-lime glass poling, where cations (mainly sodium ions) could move in the substrate towards the cathode, a decay of the current with time (at a fixed voltage) was expected due to ion migration under a blocking electrode. At the beginning of poling (first voltage step), the level of current in the pink sample was small in comparison with typical levels found in soda-lime glass under the same poling conditions. This observation is in accordance with the high electrical resistivity of the sol–gel film. After a few steps of increasing voltage, the

Table 1
Characteristics of thin sol–gel films doped with Au nanoparticles

Glass colour	Refractive index	Sol–gel film composition	Weight percent	Film thickness (nm)
Pink (type #1)	1.46	SiO_2	75.7	130
		TiO_2	3.3	
		CeO_2	5.0	
		Au	16.0	
Blue (type #2)	1.87	SiO_2	19.5	140
		TiO_2	25.9	
		CeO_2	38.6	
		Au	16.0	

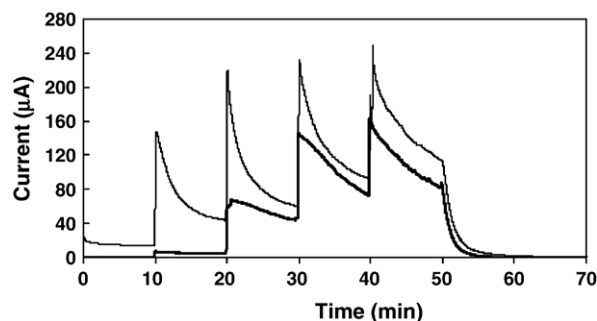


Fig. 2. Time evolutions of the current during poling at 280 °C (thick solid line: type #1 sample, thin solid line: type #2 sample) with the voltage increased in steps of 200 V (10 min each step) up to 1 kV.

current level became similar to those in soda-lime glass [9]. This fact indicates that an increase in the film's conductivity took place during poling, which can be associated with the dissolution of the gold nanoparticles. Actually, a change in the sample conductivity has been reported in the case of silver nanoparticle dissolution [5]. On the other hand, the level of the current in the blue sample was higher than in the pink sample for the same poling conditions. This behaviour can be attributed to a difference in the resistivity of the sol–gel film due to different film compositions in both types of sample.

Here, the change in the sol–gel film conductivity can weakly be attributed to the migration of gold ions because of their low mobility. Rather, we speculate that the formation of defects in the sol–gel film, such as broken bonds, can result in the increase of electron mobility.

After poling, the region in the pink sample which was delimited by the anode geometry became colourless (Fig. 3, inset), giving us an evidence of the dissolution of gold nanoparticles. As in the present case we have a high resistivity sol–gel film on top of a soda-lime-silicate glass with high ionic mobility compared to the film, we speculate that the high electrostatic field (E_{dc}) which develops in the sol–gel film during poling is able to ionize the gold clusters and to drive the released Au^+ ions away from them so that the clusters are eventually destroyed and the Au^+ ions are dissolved in the matrix.

Additionally to this “direct” ionization mechanism by the internally developed field, a secondary ionization mechanism could also be present due the emission of electrons or oxygen ions from the poled soda-lime substrate into the sol–gel film. Indeed, charge emission through the anodic surface of poled soda lime has been reported [10–12]. The structurally changed surface of the poled soda-lime substrate could act as a source of negative charges that bombard the film on their way to the anode. This charge migration would ionize the film and also strike the nanoclusters, paving the way to the emission of

positive gold ions into the matrix. On the other hand, because the sol–gel film has high resistivity when compared with the soda-lime substrate, most of the applied voltage drops across the film at the beginning of poling and only a small amount of voltage drops at the substrate. Under this condition, the charge bombardment mechanism is expected to give only a minor contribution to the ionization process when compared with the direct ionization mechanism.

The optical absorbance spectra ($A = -\log(I_{out}/I_{in})$) of poled and unpoled regions of the pink sample and blue sample were measured. In the case of the pink sample, complete suppression of the main absorbance band in the visible range could be observed after poling as an evidence of the bleaching effect (Fig. 3). The peak of the suppressed absorption band was located at 520 nm which coincided with the surface plasmon resonance of Au particles in the pink sample [13]. The absorption band centred at 376 nm was attributed to Fe^{3+} content in the host material. In the case of the blue sample, the absorbance band in the visible range was not suppressed after poling, i.e. no bleaching effect was observed. This striking difference in the responses of the pink sample and blue sample to thermal poling is believed to be due to variations in the film's resistivity and dielectric constant with the film's composition. In this way, a larger electrostatic field is thought to develop in the pink sample than in the blue one under the same poling conditions.

The electrostatic field E_{dc} induced by poling in the pink sample can be estimated by assuming a uniform distribution of the field across the 130-nm film thickness. For the lowest value of the applied voltage (200 V), the value of E_{dc} is estimated to be equal to 5×10^9 V/m. Based on this estimate, it follows that the electric field strength which was needed to dissolve Au nanoparticles was one order of magnitude higher than the one which was needed to dissolve Ag nanoparticles ($E_{dc} \approx 1$ kV/ $5 \mu m = 2 \times 10^8$ V/m from Ref. [5]). This result is consistent with the expectation that gold clusters are more difficult to ionize than silver clusters. Indeed, based on the standard electrode potential E^0 , the degree of metal ionization at room temperature is smaller for silver (0.80 V) than for gold (1.83 V), which indicates that it is more difficult to ionize gold than silver [14].

The mechanism of gold cluster dissolution is suggested to be based on the presence of the high electrostatic field which develops during poling and ionizes the cluster. The mechanism is as follows: electrons are ejected from the ionized cluster and extracted at the anode, the positively charged gold ions are expelled from the cluster by Coulomb forces and carried away in the matrix, leaving the gold cluster uncharged behind [15]. This process cycles until the cluster is destroyed and the gold ions are dissolved in the matrix.

4. Conclusions

In conclusion, poling-assisted bleaching of Au-doped nanocomposite sol–gel glass film on top of ion-conducting glass substrate has been demonstrated. The sol–gel film composition played an important role in the dissolution of the gold nanoparticles by the electrostatic field which developed during poling. This result opens the possibility to use other metal

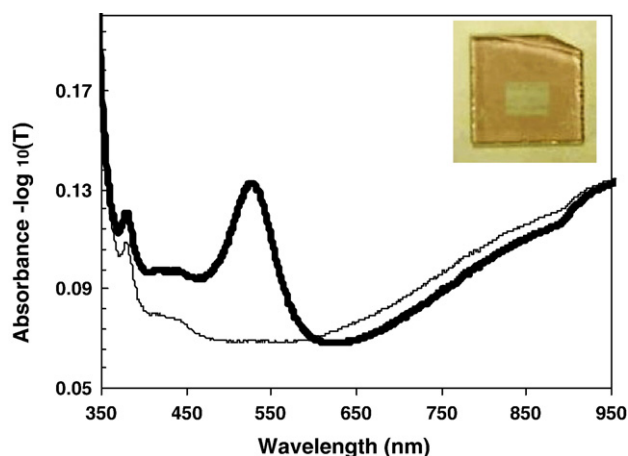


Fig. 3. UV-IR absorbance spectra of the pink sample before (thick solid line) and after (thin solid line) poling. The peak at 520 nm in the pristine sample is due to the surface plasmon resonance of gold nanoparticles and is completely bleached after poling. Inset: photograph of type #1 (pink) sample after poling at 280 °C, +1 kV. The bleached (i.e. colourless) region under the anode is well defined by the electrode size. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

particles such as platinum and palladium in order to tailor the region of transparency of glasses with various compositions, opening the perspectives towards new surface plasmonic devices.

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